ANALYSIS OF PERU MARGIN SURFACE SEDIMENTS BY PY-MS

By

T.I. Eglinton[1], M.A. McCaffrey[1]#, H. Huai[2] and H.L.C. Meuzelaar[2].

[1]Dept. of Chemistry, Woods Hole Oceanographic Institution, Woods Hole MA 02543.

[2]Center for Micro Analysis and Reaction Chemistry, EMRL, University of Utah, Salt Lake City, UT 84112.

INTRODUCTION

In off-shore Peru high sedimentary organic carbon contents are a direct consequence of the extremely high primary productivity (ca. 1000g Carbon $m^{-2}.yr^{-1}$)[1] which, in turn, is supported by the upwelling of nutrient-rich waters near the coast. Diatoms represent the major phytoplankton type and give rise to sediments dominated by biogenic silica and planktonic organic matter. The remineralisation of this large flux of organic matter to the bottom waters and sediments results in oxygen depletion over large areas of the shelf which, in turn, promotes organic carbon preservation in the underlying sediments. Sulfide from sulfate reduction is prevalent in the bottom waters[2] and with a limited availability of iron (due to the dominant biogenic input coupled with a very low influx of detrital sediments) the excess sulfide is available for reaction with the organic matter. As a result high organic sulfur concentrations are found in the sediments[3].

The coastal Peru upwelling region is believed to be a modern analogue to the depositional environments of petroleum source rocks such as the Miocene Monterey Formation of the California Borderland[4]. Because organic matter alteration pathways in surface sediments ultimately influence kerogen type and eventual petroleum yield, there has been interest in characterizing surface sediments such as those off-shore Peru. Lipid[5-10], carotenoid[11] and amino acid[12] constituents as well as general biogeochemistry[1,13] have been studied previously. However, studies of the macromolecular components of the sediments have been less extensive[3,14].

This paper describes results from Py-MS analyses of sediment samples obtained from discrete intervals in a 1-meter core obtained from the upper continental shelf of the Peru Upwelling region. Factor and discriminant analysis of the Py-MS data revealed several distinct changes within this 1-meter section.

EXPERIMENTAL

Sample Recovery and preparation

Fifteen sediment samples obtained from a single ca. 1-meter box core were used for this study. The core ("SC3") was taken during a cruise of the R/V Moana Wave in 1987, and was retrieved from Station 4 (15°06.16'S, 75°42.09'W) at a water depth of 253m (within the prevailing oxygen minimum zone). Further information concerning the location and detailed geochemistry of these samples are provided elsewhere[15]. General geochemical descriptions of the samples are listed in Table 1.

Present address: Chevron Oil Field Research Company, Richmond CA 94802

Wet sediment samples were pre-extracted with isopropanol, followed by a methanol-chloroform mixture (to remove soluble lipid components) and subsequently air-dried prior to further analysis. Organic carbon and nitrogen measurements were made on de-carbonated sediment samples using a Perkin Elmer 2400 CHN analyzer.

Pyrolysis-Mass Spectrometry (Py-MS)

Similar experimental and mathematical procedures to those described by Metcalf et al.[16] were adopted for the present investigation. Briefly, dried samples were suspended in methanol (5 mg/ml) and approximately 75 μg of sediment was applied to each wire (Curie temperature, 610°C). Uniform sample coating was achieved by rotation of the wires during air-drying.

Py-MS was performed on an Extranuclear 5000-1 quadrupole MS system described by Meuzelaar et al.[17]. Pyrolysis was started 30 s after introduction of the sample into the mass spectrometer. Py-MS conditions were as follows: temperature rise time 5s, total heating time 10s, electron energy 12 eV, mass range m/z 20-300, scanning rate 2000 amu/s, total number of scans acquired = 70. Each sample was analysed in triplicate.

Multivariate Statistical Analysis

Multivariate statistical analysis of the Py-MS spectra was performed using the SIGMA (System for Interactive Graphics-oriented Multivariate Analysis) program described by Windig and Meuzelaar [18].

The stored Py-MS data were firstly calibrated and normalized. Subsequently, factor analysis was performed, followed by discriminant analysis. Discriminant analysis was applied on the first seven factors (explaining 82% of the total variance, see Table 2) selected on the basis of Cattell "scree break" criterion[19]. As applied here, discriminant analysis involved an orthogonal rotation of factor space aimed at maximising outer/inner variance ratios. Outer variance is a measure of the differences between groups of spectra; inner variance is a measure of the internal variation within replicates as a consequence of experimental scatter or sample heterogeneity. The results are expressed in terms of discriminant scores which provide a quantitative measure of the differences, and in the form of numerically-extracted discriminant spectra[20], which give information about the mass intensity changes involved. The pyrolysis data are interpreted in terms of chemical "components" by means of the "variance diagram" (VARDIA) technique, a method developed for numerical analysis of unknown mixtures[21]. The basic principle is that the VARDIA plot shows how strong the correlated behavior of all mass variables is in all possible directions (in steps of 10°). Directions in the discriminant space which can be attributed to such chemical components are called "component axes".

RESULTS

Figure 1 shows averaged Py-MS spectra of samples from four intervals within the core. In general, the spectra are rather similar, being dominated by low mass ions and containing maxima at similar m/z values. Major series include ions those due to sulfur compounds such as H_2S (m/z 34), S_2 or SO_2 (m/z 64), HSSH (m/z 66), and S_4 (m/z 128), as well as sugar products (e.g. m/z 114, 126, 128, 144). Other mass peak patterns reflect contributions from aliphatic hydrocarbons and alkylaromatics (alkylphenols and alkylbenzenes).

Despite the similarity between the traces, factor and discriminant analysis allowed a number of distinctions to be made between the samples studied. Table 2. lists results from factor analysis of the data matrix including all samples and mass peaks. Slightly over 50% of the total variance is explained by the first factor, with the second and third factors accounting for a further 17% and 5% respectively.

The results from discriminant analysis of the data set are presented in Table 3 and Figure 2. Tighter clustering of the replicates and better separation between different samples is observed after discriminant

rotation than in the original score plots (not shown here). It is apparent that Discriminant function 1 (DF1) strongly reflects sediment depth, as clearly revealed by a cross-plot of these two parameters (Fig. 3). Fluctuations which are not directly related to depth are manifested in DF2 (non-depth-related variations are also evident in DF's 3 & 4, Fig. 2b). In addition, three or four "sub-groups" may be identified in Figure 2a (as indicated by the circles). The spectra shown in Figure 1 each correspond to one of these four groups.

In order to determine the chemical variations responsible for these fluctuations, variance diagrams were constructed in which the DF's are kept orthogonal to one another, but may be rotated (in 10° increments) so as to study axes which most clearly reflect differing "chemical components". This is shown in Figure 4(a) in DF1/DF2 space, in which three separate "components" may be identified. A fourth was identified in DF3 (Figure 4b). Mathematically-extracted "discriminant spectra", obtained for each of these chemical "components" from rotation within this framework are presented in Figure 5. Component "A" (DF1 & DF2, 10°) shows a typical pattern derived from sugar moieties. Component "B" (50°) shows strong influence from sulfur-derived compounds as well as some higher mass components (m/z 155, 159, 173 etc.). Component "C" (320°) contains, in addition to sulfur compounds, alkylaromatics including alkylbenzene and phenolic compounds. Component "D" from DF3 & DF4 (70°) contains mass peaks possibly characteristic for terpenoid component(s).

From these data we may conclude that the depth-related variation in "kerogen" reflected in DF1 is primarily the result of a decrease in sugar-containing components together with a corresponding increase in sulfur-containing and alkylaromatic components. The latter is consistent with current concepts concerning sulfur incorporation into organic matter during early diagenesis[22,23]. Other fluctuations independent of depth are presumably a consequence of variations in conditions at the time of deposition. The chemical components responsible for these latter variations are yet to be fully interpreted.

CONCLUSIONS

Py-MS in conjunction with multivariate statistical analysis of Peru margin sediments has allowed several insights to be made into the formation and transformation of macromolecular organic matter during early diagenesis. Distinctive depth-related changes in chemical composition were observed, including a loss of sugar-containing moieties and an increase in sulfur content. Features reflecting fluctuations due to other influences on organic matter composition were also detected. This study demonstrates the utility of this approach as a rapid method for providing information on macromolecular sedimentary organic matter composition.

ACKNOWLEDGEMENTS

REFERENCES

1. Reimers C.E. and Suess E. *Coastal Upwelling and its sediment record, Part B.* (eds. J. Theide and E. Suess). pp. 311-337. Plenum, New York (1983).
2. Fossing H. (1990) *Continental Shelf Research*. In press.
3. Patience R.L., Clayton C.J., Kearsley A.T., Rowland S.J., Bishop A.N., Rees A.W.G., Bibby K.G. and Hopper A.C. *Proceedings Scientific Results, Leg 112, Ocean Driling Program.* (Eds. E Suess, R von Huene et al.) pp. 135-153. ODP College Station, Texas (1990).

4.   Soutar A., Johnson S.R. and Baumgartner T.R. *The Monterey Formation and related siliceous rocks of California.* pp. 123-147. SEPM Los Angeles (1981).

5.   Volkman J.K., Farrington J.W., Gagosian R.B. and Wakeham S.G. *Advances in Organic Geochemistry, 1981* (eds M. Bjoroy *et al.*) pp. 228-240. Wiley and Sons (1983).

6.   Wakeham S.G., Farrington J.W. and Gagosian R.B. *Org. Geochem.* **6**, 203-215 (1984).

7.   Volkman J.K., Farrington J.W. and Gagosian R.B. *Org. Geochem.* **11**, 463-477 (1987).

8.   Farrington J.W., Davis A.C., Sulanowski J., McCaffrey M.A., McCarthy M., Clifford C.H., Dickinson P. and Volkman J.K. *Org. Geochem.* **13**, 607-617 (1988).

9.   McCaffrey M.A., Farrington J.W. and Repeta D.J. *Org. Geochem.* **14**, 61-68 (1989).

10.   McCaffrey M.A, Farrington J.W. and Repeta D.J. *Geochim. Cosmochim. Acta* **54**, 1713-1724 (1990).

11.   Repeta D.J. and Gagosian R.B. *Geochim. Cosmochim. Acta* **51**, 1001-1009 (1987).

12.   Henrichs S.M., Farrington J.W. and Lee C. *Limnol. Oceanogr.* **29**, 20-34 (1984).

13.   Henrichs S.M. and Farrington J.W. *Limnol. Oceanogr.* **29**, 1-19 (1984).

14.   Whelan J.K., Kanyo Z., Tarafa M. and McCaffrey M.A. Pre-print (1990)

15.   McCaffrey M.A. Ph.D. Thesis. MIT/WHOI, WHOI-90-29 (1990).

16.   Metcalf G.S., Windig W., Hill G.R. and Meuzelaar H.L.C. *Int. J. Coal Geol.* **7**, 245-268 (1987).

17.   Meuzelaar H.L.C., Haverkamp J. and Hileman F.D. *Pyrolysis Mass Spectrometry of Recent and Fossil Biomaterials; Compendium and Atlas.* Elsevier, Amsterdam 294 pp. (1982).

18.   Windig W. and Meuzelaar H.L.C. *Proceedings of the 34th ASMS Conference.* Cincinnati, pp. 64-65. (1985).

19.   Cattell R.B., *Multivariate Behavioral Research.* **1**, 245-276 (1966)

20.   Windig W., Kistemaker P.G. and Haverkamp J. *J. Anal. Appl. Pyrol.* **3**, 199-212 (1981).

21.   Windig W. and Meuzelaar H.L.C. *Anal. Chem.* **56**, 2297-2303 (1984)

22.   Sinninghe Damsté J.S. Eglinton T.I., de Leeuw J.W. and Schenck P.A. *Geochim. Cosmochim. Acta* **53**, 873-889 (1989).

23.   Sinninghe Damsté J.S., Rijpstra W.I.C., Kock-van Dalen A.C., de Leeuw J.W. and Schenck P.A. *Geochim. Cosmochim. Acta* **53**, 1343-1355 (1989).

Table 1 Geochemical Description of Samples of Peru Sediments from core SC3.

Sample #	Depth (cm)	TOC (%)	%N	Dry wt./wet wt.
1	4-5	11.10	1.26	0.0699
2	9-10	9.20	1.07	0.0640
3	16-17	9.17	1.17	0.0765
4	27-28	9.79	1.19	0.0831
5	30-31	11.02	1.26	0.1115
6	38-39	8.67	1.21	0.1381
7	42-43	8.19	1.03	0.0978
8	46-47	6.19	0.71	0.0859
9	55-56	7.67	0.88	0.1026
10	65-66	7.67	0.92	0.2415
11	70-71	6.81	0.77	0.1467
12	75-76	6.94	0.79	0.2610
13	77-78	7.61	0.87	0.2532
14	85-86	7.00	0.75	0.1717
15	94-96	7.09	0.77	0.1741

Table 2 Results from Factor analysis of normalized Py-MS data.

Factor	Eigen Val.	% Total Var.	% Cum. Var.
1	118.01	50.87	50.87
2	39.91	17.20	68.07
3	12.07	5.20	73.27
4	8.27	3.57	76.84
5	4.94	2.13	78.97
6	3.92	1.69	80.66
7	3.78	1.63	82.29

Table 3 Results from Discriminant analysis of Py-MS data.

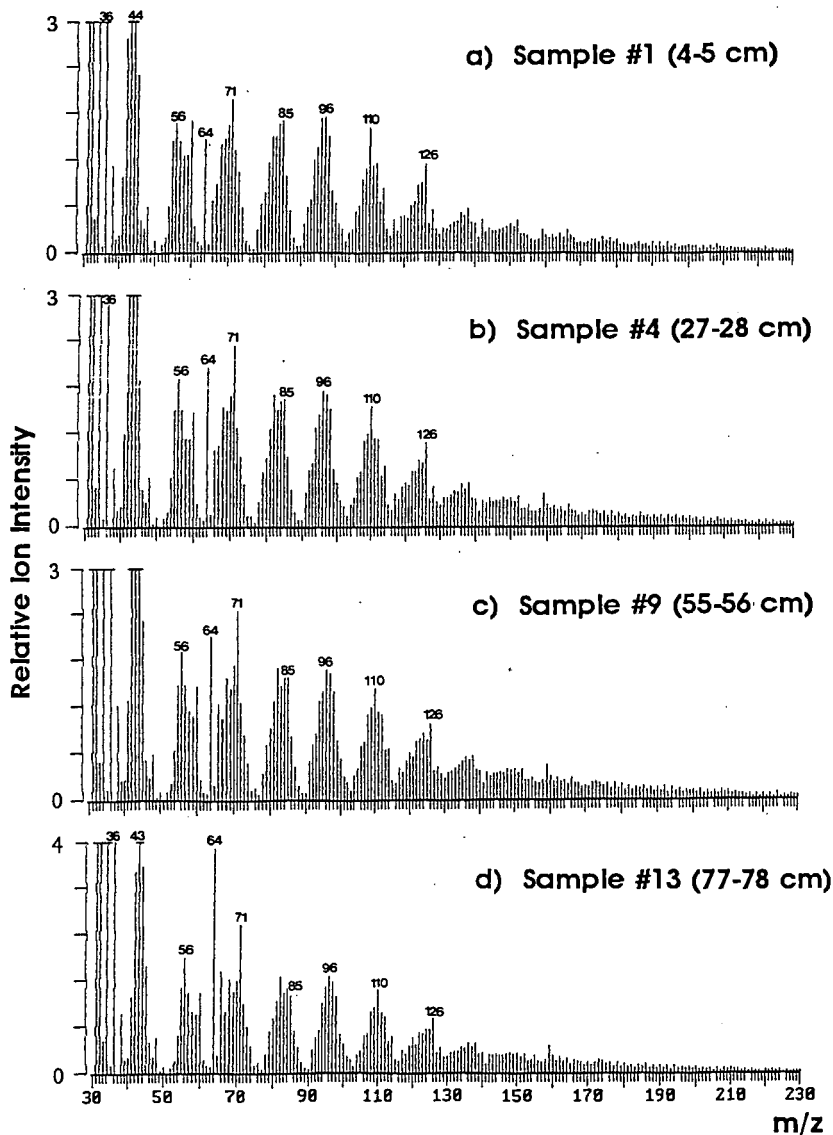| Discr. Func.	Eigen Val.	% Outer Var.	% Total Var.	Canonical Corr.
1	40.30	61.88	17.10	0.988
2	11.57	17.77	4.92	0.959
3	7.79	11.96	9.55	0.941
4	3.84	5.89	38.16	0.891
5	1.16	1.77	4.31	0.732
6	0.29	0.45	5.70	0.475
7	0.18	0.27	2.55	0.388

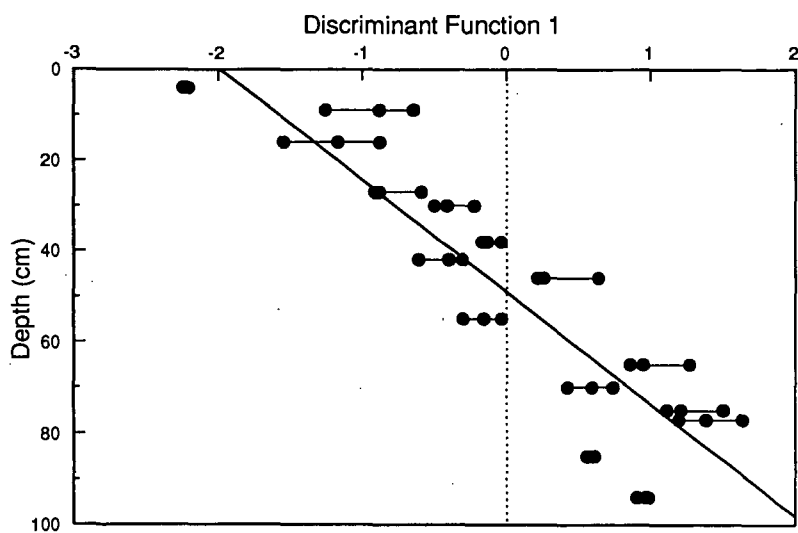Figure 1. Averaged Py-MS spectra from triplicate analyses of four extracted Peru sediments from core SC3.

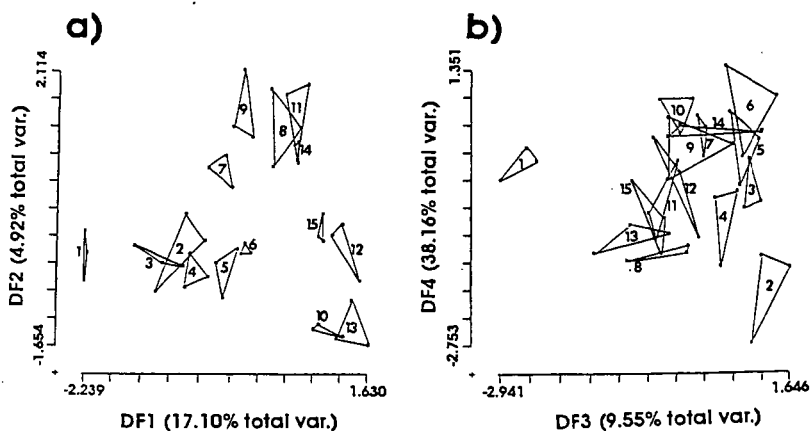Figure 3. Plot of Discriminant Function 1 versus Depth (cm)

Figure 2. Score plot from Discriminant analysis of normalized Py-MS data:
(a) Discriminant Function 1 versus Discriminant Function 2;
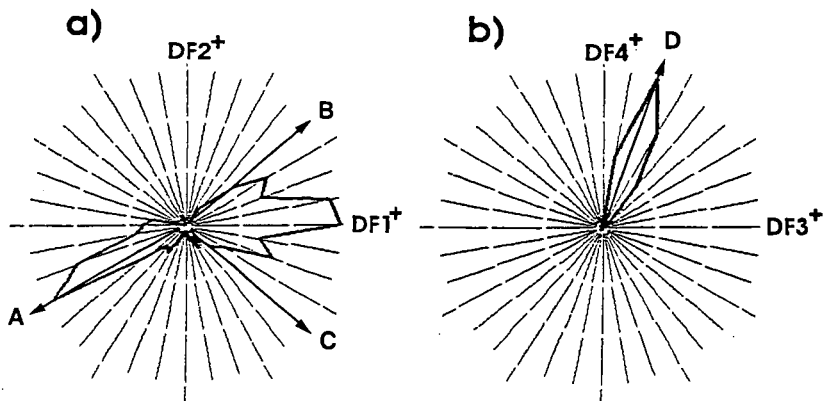(b) Discriminant Function 3 versus Discriminant Function 4.

Figure 4. Variance diagram (VARDIA) showing presence of four discrete chemical component axes in the space spanned by discriminant functions 1 and 2 (a) and 3 and 4 (b).
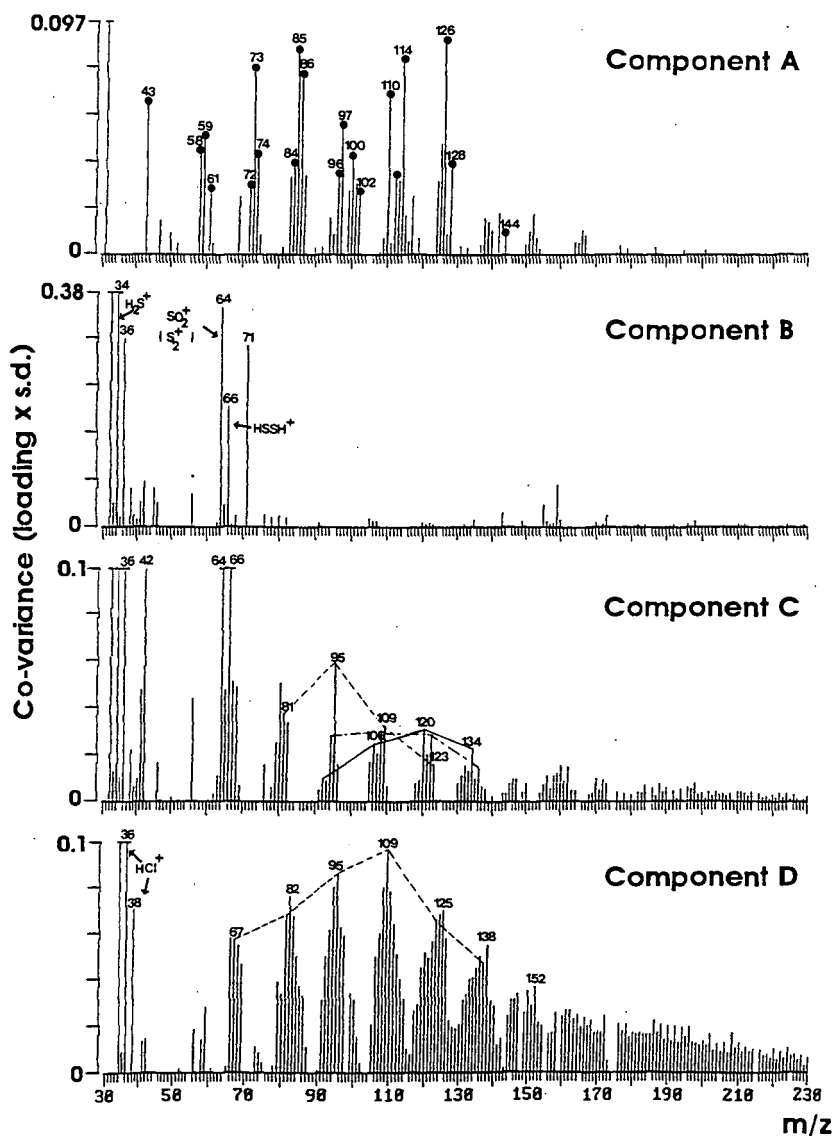
Figure 5. Mathematically-extracted "Discriminant Spectra"
of Chemical Components A, B, C and D.